NONTOXIC WATERY SOLUTION AGAINST FREEZING AND CORROSION AND THE REGENERATOR FOR THE UTILIZED ANTIFREEZE

Field of the art

The present invention is related to the field of cooling [[an]] internal combustion engines passenger and truck vehicles), and ~~also cooling of~~ other cooling and heating systems where heat ~~exchanger is~~ exchangers are used. Precisely, this invention is related to field of fluids – liquids for cooling the operating engine, i.e., to the anti-freezing and anticorrosive agent composition ~~(antifreeze is the word originating from English language and as such it is adopted in our language, and literally it means anti ice, anti freezing)~~ and [[to]] the ~~composition of~~ antifreeze regeneration agent, primarily glycerin-based, ~~and~~ which are ~~thereat~~ absolutely nontoxic~~, and which comprise variety of other components, depending on application in particular weather conditions, i.e., conditions of application~~.

~~According to international patent classification (MKP/IPC) inventions belong to class F 01 P 3/00, class B 60 K 11/02, by which the cooling of machines (engines) or other cooling and heating systems are generally defined, i.e., cooling by fluid liquids, which are added to stop the corrosion. Beside the said class, inventions belong to class C 09 K 005/00, by which devices and apparatus in vehicles are defined such as to facilitate cooling of operative units with cooling liquid.~~

~~Technical Problem~~

The technical problem which is solved ~~by inventions~~ is how to obtain ~~composition –~~ an anti-freezing agent useful in open and closed cooling systems, to obtain nontoxic liquid (fluid) for heat exchange ~~according to the invention,~~ and at the same time to obtain anticorrosive protection in cooling system for all metals, especially for aluminum engines or parts of the engine, i.e., how to obtain ~~agent~~ composition that will be used for regeneration and modification of anti-freezing and anti-corrosive agent.

State of the art

There are known cooling fluids which are used in the cooling systems of internal combustion engines, in open and closed cooling systems, which do not freeze at temperatures from -30°C to -40°C. Most of these fluids are ~~in market~~ marketed under the name antifreeze~~, and among domestic manufacturers the major are: Kotrman, NIS-Naftagas, Petrohemija-Pančevo, in Bosnia and Herzegovinia – Optima Modriča, etc. There are known great world manufacturer among which major are BASF from Germany, Preston from SAD, and many other~~.

Mainly, the compositions are specifically formulated with ethylene glycol or propylene glycol, or with derivates thereof and include additives which inhibit and reduce corrosion of the cooling system. ~~Very important is to~~ To develop specific cooling agent formulations[[,]] is important because, with appearance of engines with higher performances, especially heavy-duty diesel engines, there are growing numbers of ~~these engines~~ engine components which are produced from a variety of materials to reduce[[,]] weight and enhance efficacy. Therefore, specific additives are selected so to provide special advantages, such as providing protection for one or more selected materials. However, these additives are often selected in such a way that their beneficial properties are mutually supplemented. Despite formulating ~~specificity of these~~ specific cooling agent compositions, advantages that are connected to many additives may be disturbed[[,]] because many drivers pour hard water in the cooling system. Hard water may be added either after initial filling of the cooling system or during the service, since drivers themselves, but also workers in relevant services add ordinary water in the cooling system (i.e., they change water that ~~have~~ has been lost by evaporation and the like).

However, in many parts of the world there is no available suitable water for use in ~~the~~ cooling systems. Hard water contains ~~certain number of~~ minerals, mostly calcium, magnesium and iron salts. These minerals may contribute to loss of efficacy and to reduce lifetime of cooling agent composition. The loss may be especially adverse for heavy-duty diesel engines that may pass ~~away~~ over ~~20 000~~ 20,000 kilometers per month. Non-effective cooling agent composition may reduce engine lifetime, clog internal passages in the cooling system, contribute to cylinder liner corrosion and clog water pump~~, where all that have as a result an expensive engine repair~~.

~~Surely, the tendency of~~ The trend toward reducing noxious ~~gasses~~ emission has ~~as a~~ resulted in some progress in engine emission technology, and that progress may induce change of usual ethylene glycol and/or propylene glycol bases which have been for almost one century the main carrier for engine antifreeze formulations. New engine components, especially devices for exhaust ~~gasses~~ gas recirculation (EGR), ~~produce~~ result in much bigger thermal stress to the engine cooling agent. Ethylene glycol and propylene glycol oxidation may be drastically accelerated, which results in cooling agent that becomes ~~improper~~ unacceptable for ~~continuous~~ continued usage, even in such short time intervals as several months. Therefore, manufacture is moving toward ~~formation~~ engine cooling agents which operate in longer time intervals, i.e., toward ~~formation~~ agents ~~by~~ which ~~it will be~~ are possible to regenerate and/or optionally to modify ~~wasted cooling agent (antifreeze)~~.

Because of what is stated but also because of number of other reasons, there is continuous need for improvement of cooling agent compositions and for improved processes of corrosion reduction which are connected with cooling agent compositions. This invention represents such improvement and it provides great number of different advantages.

~~There are relatively a great number of patent applications, i.e., approved patents which describe antifreeze, i.e., cooling agent. Generally, according to herein applied invention, difference is in that their basic bases are mostly some other chemicals and that they use less additives, and in different ration, where for most of them it could be said that they don't have anti-corrosive effect and almost all are toxic.~~

- Patent application EP 1010740 A1 discloses solution which comprises glycerol as a basis, but which comprises only 4 additives;
- Invention from patent application published under number WO 03/040254 A1, as basic basis has alcohol, and parts of patent application which are related to glycerin base also have lesser number of additives;
- Inventions from patent DE 1125407, 569771, 1 125 407 are made from mixture of propylene glycol (i.e., glycol – but it is not said which) and glycerol therefore anti-corrosive protection is not sufficient;
- In patent application published under number WO 02/08354 A1 antifreeze is made with basic base of monoethylene glycol of about 69% with small amount of

glycerol, and therefore there have not been accomplished sufficient anti-corrosive protection;

- In patent DE 10163337, antifreeze is made with basic base of monoethylene glycol of about 69% with small amount of glycerol, and therefore there have not been accomplished sufficient anti-corrosive protection;
- In patent number 25-40 251, antifreeze is made with basic base of propylene glycol;
- In patent application 048 430 A1, antifreeze is made with monopropylene glycol and ethylene glycol;
- In patent number U.S. Pat. No. 4,000,079 A, antifreeze is made with glycol and other anti-corrosive protection agents;
- In patent number US 455,248 A, antifreeze is made with glycol;
- In patent application 4,404,113 A, antifreeze is made with basic base of 94% monoethylene glycol, and alcohol glycerol have been used as an inhibitor, with other additives;
- In patent number US 489,391, antifreeze is made by using glycol, i.e., ethylene glycol to ~~94,74~~ 94.74%, but there have not been used enough additives;
- In patent application U.S. Pat. No. 5,387,360 A, antifreeze is made with basic base of ethylene glycol to ~~92,489~~ 92.489%;
- In patent application US 2003/0198847 A1, inhibitor protection is made for more types of basic crude materials which are used for antifreeze preparation, and among them glycerol.

Disadvantages of ~~all mentioned, but also~~ the foregoing, as well as many other solutions, ~~is~~ are that they are toxic; their lifetime is limited to ~~the most~~ two years, they have ~~not~~ insufficient inhibitory protection, they weaken alkali stocks, and their pH value is ~~small~~ too low – about ~~6,2-7,2~~ 6.2 to 7.2 (it must be between ~~9,5-11,5~~ 9.5 and 11.5 according to ASTM standard~~—USA standard~~). ~~Inventions applied herein~~ The present inventions meet ASTM standards.

~~Presentation of Essence~~ Description of the Invention

This invention is related to new antifreeze/anti-freezing (and anti-boiling) ~~agent~~ composition with a non-toxic ~~basis~~ base in water solution in concentration to 96%~~, which can be~~

~~used immediately~~. This antifreeze may be used concentrated or diluted with distilled water. It is non-toxic.

~~Here is also presented the composition of~~ Also described is an anti-corrosive inhibitor in water solution for wasted antifreeze, which ~~beside the composition of antifreeze alone makes invention conception unique, in sense of its using~~ can be used on the one hand for antifreeze production and on the other for regeneration and modification of that antifreeze[[,]] when that antifreeze is wasted.

~~Applicant noted that detailed~~ Detailed descriptions of both inventions are given below, but their specific compositions will be dependent only of application conditions (type of ~~the~~ vehicle, ~~i.e.,~~ other agents, climatic conditions, etc.~~and other~~). In that sense given compositions are not limiting.

First, anti-freeze and anti-corrosive ~~agent~~ composition (antifreeze) will be ~~represented~~ described. This composition ~~base makes~~ includes distilled (softened) water, non-toxic base (glycerol), and suitable inhibitors. By mixing these ingredients, anti-freezing and anti-corrosive agent for engines is obtained, which is ecologically correct, biodegradable, non-toxic and not harmful for natural resources, does not pollute soil and water, not toxic for humans, fishes, animals and pets, and ~~thereat it~~ successfully protects engines (protects system against freezing and corrosion, against forming plaque and foam in the system, and ~~rises~~ increases the boiling point above 120°C).

For composition of anti-freeze and anti-corrosive agent, following additives are used as inhibitors:

A) Additives as inhibitors
   1. Glycerol
      - chemical formula $C_3H_8O_3$
      - ~~quality min. 98,0% (99,5%)~~ minimum purity of 98.0% (99.5%)
   2. Water – soften or distilled
   3. Benzotriazole – effective inhibitor against corrosion of metals in neutral solution
   4. ~~Three-ethanol-amine~~ Triethanolamine ($(HOCH_2CH_2)_3N$) – an inhibitor against corrosion of iron and steel ~~in watery solution)~~

5. ~~Sodium tetraborate~~ Sodium tetraborate
   - chemical formula $Na_2B_4O_7$
   - an inhibitor for several metals, aluminum and their alloys
6. ~~Sodium nitrate~~ Sodium nitrate
   - chemical formula $NaNO_3$
   - protects several metals
7. ~~Sodium nitrite~~ Sodium nitrite
   - chemical formula $NaNO_2$
   - necessary concentration depends on corrosion conditions and water content in formulation
8. ~~Sodium sul~~ Sodium sulfite
   - chemical formula ~~(without water~~ $NaSO_3$ (without water) or ~~($naSO_3$)$_7$$H_2O$~~ $NaSO_3 \cdot 7H_2O$
   - ~~in this formulation, it's~~ a good inhibitor for magnesium, aluminum or their alloys in alkali environment or in ~~watery~~ aqueous solution of glycerol.
9. ~~Potassium sulfide~~ Potassium sulfate
   - chemical formula K_2SO_4
   - ~~min.~~ minimum purity of 99% ~~quality~~
   - ~~solution~~ easy ~~soluble~~ solubility in water
   - in this formulation, an inhibitor of aluminum, magnesium and their alloys
10. ~~Sodium chromate~~ Sodium chromate
    - chemical formula in acids ~~HNO_3, H_3PO_4 and H_2SO_4~~ (Na_2CrO_4)
    - corrosion inhibitor of steel, cast iron, aluminum, ~~cooper, zink and messing~~ copper and zinc in ~~watery~~ aqueous solution of this formulation
11. ~~Sodium benzoate~~ Sodium benzoate
    - chemical formula ~~$C_6H_5SO_6Na$ or ($C_7H_5O_2Na$[])~~]
    - corrosion inhibitor of steel in water solutions and well preserved pH value and alkalis
12. ~~Calcium cyanamide~~ Calcium cyanamide
    - in this formulation, corrosion inhibitor of steel in watery solutions and solutions of salts
13. ~~Sodium hydroxide~~ Sodium hydroxide
    - suitable for aluminum protection as well as for the preserving of alkali reserve and pH value between 9-11

14. ~~Polymark polycaroxilate BASF,~~ Polycarboxylates which are soluble in ~~watery~~ aqueous and alcohol solutions~~. In this invention is marked~~ such as ~~SOKALON®~~ SOKALAN® CP-12S or CP-10 (BASF). In this formulation, ~~well applicable is~~ ABC COBLEX's ~~polycarboxilate, too~~ polycarboxylates also are useful.

15. ~~Sodium metaborate~~ Sodium metaborate
   - chemical formula ~~(calculated on B2O3)+2+3+4~~ $NaBO_2$ with application in concentrations of from ~~0,5-5 mass~~ 0.5 to 5 parts by weight
   - an inhibitor for metals in formulation of nontoxic antifreeze based on glycerol

Process for obtaining antifreeze ~~is conducted through~~ involves several phases. First, distilled water preparation is performed (softened to I degree), or totally distilled and free from all minerals and contamination. Mixing is performed with polyvalent alcohol (glycerol) at temperatures of 80-90°C, with continuous agitating until homogenization is completed. Basic base [[–]] to crude material ~~rations,~~ ratios may be different dependent on what is desired to be designed. Main crude material may be 66:34, 70:30, 80:20, and different ratios are possible. In said ratios it is necessary to ~~left~~ leave space for inhibitor (modifier, emulsifier) ~~(whose composition will be presented below in this application) with its participation~~ in quantitative content ~~with~~ of 10-20%. After that, heating is continued with the same temperature and agitating until homogenization (unification) of the product completed. ~~Against~~ To inhibit foaming, silicate oil is added in small concentrations (0.004 to 0.009%) ~~of 0,004-0,009%~~. Additionally, high quality and also non-toxic dye is added, ~~that is~~ i.e., the type used for nutrition or cosmetics. Final product is a light green or light blue liquid. Dye is added ~~to fluid to indicate is there any liquid in the system, and~~ because the thus obtained liquid is white and clear.

In other words, the ~~performing of the~~ production process ~~is~~ involves the following: the substances-additives in group A ~~is mixing~~ are mixed, then, ~~there is a mixing of~~ additives from group B are mixed, and finally, ~~the mixing of~~ additives from group C are mixed. After that, on the same sequence as above, there is mixing of groups, one by one, ~~on the~~ at a temperature of 80°C~~, using a mixer with small numbers of revolutions,~~ and at about 100-200 revolutions per minute.

The mixed additives are ~~mixing~~ mixed into the basic substance, according to tables and sequence, after the preparation of additives. The ~~relations is the following~~ relative proportions

are as follows: for ~~minus~~ temperature of -25°C, the additives from ~~table~~ "A" in Table A are used with 38% of ~~basic substance~~ base (glycerol);[[,]] for temperature of -35°C, the formulation "B" from ~~table "A"/B~~ Table A is ~~mixing~~ used with 48% of ~~basic substance,~~ base; for temperature of -55°C the formulation "C" from ~~table "A"/C~~ Table A is ~~mixing~~ used with ~~the~~ 60% of ~~basic substance,~~ base; and for the ~~minus~~ temperature ~~over~~ of at least -65°C, the ~~there is a mixing of~~ formulation "D" from ~~table "A"/D~~ Table A is used with ~~the~~ 88% of ~~basic substance~~ base. All these combinations can maintain the temperature from 110°C ~~till~~ to 160°C ~~in plus~~.

Thus obtained antifreeze is non-toxic, biodegradable and ~~it~~ does not pollute the environment. Additionally, this is a very durable (resistant) fluid – it can be used for more than six years or 350,000 km in the cooling system. It is ~~used~~ useful for temperatures between from -70°C to +160°C, dependent on concentration[[,]] (max. 96%). ~~There should be noted that at~~ At low temperatures this fluid does not change to solid, but to frail, delicate crystals that do not ~~make~~ create pressure ~~to~~ on the walls of the engine, pipes and other parts, ~~but break out those parts,~~ and during engine ignition those crystals are readily heated and melted without damaging engine and other cooling system structures.

Following Table A shows different antifreeze composition variants, and therewith particular formulations will be dependent on climate and application conditions, and it is provided for use at temperatures from -15° to -70°C and from +110° to +160°C.

TABLE ~~"A"~~ A

FORMULATION	A	B	C	D
Components in %	(additive content in the formulation)			
A)				
- Distilled water	~~32,40~~ 32.40	~~24,00~~ 24.00	~~24,00~~ 24.00	~~25,00~~ 25.00
- Triethanolamine	~~0,60~~ 0.60	~~1,00~~ 1.00	~~3,10~~ 3.10	~~3,60~~ 3.60
- Polycarboxylate	~~0,60~~ 0.60	~~1,00~~ 1.00	~~2,60~~ 2.60	~~3,40~~ 3.40
- Benzotriazole	~~0,50~~ 0.50	~~1,50~~ 1.50	~~3,20~~ 3.20	~~4,80~~ 4.80
B)				
- Distilled water	~~55,00~~ 55.00	~~48,00~~ 48.00	~~39,00~~ 39.00	~~33,00~~ 33.00
- Sodium tetraborate	~~0,20~~ 0.20	~~0,40~~ 0.40	~~0,60~~ 0.60	~~0,80~~ 0.80
- Sodium nitrate	~~0,20~~ 0.20	~~0,30~~ 0.30	~~0,40~~ 0.40	~~0,45~~ 0.45
- Sodium nitrite	~~0,15~~ 0.15	~~0,25~~ 0.25	~~0,35~~ 0.35	~~0,45~~ 0.45
- Sodium ~~sulphide~~ sulfide	~~0,10~~ 0.10	~~0,25~~ 0.25	~~1,10~~ 1.10	~~1,40~~ 1.40
- Potassium ~~sulphide~~ sulfide	~~0,13~~ 0.13	~~0,90~~ 0.90	~~2,20~~ 2.20	~~2,90~~ 2.90
- Sodium chromate	~~0,10~~ 0.10	~~0,20~~ 0.20	~~0,65~~ 0.65	~~1,00~~ 1.00
- Sodium benzoate	~~0,10~~ 0.10	~~0,20~~ 0.20	~~0,35~~ 0.35	~~0,45~~ 0.45
- Sodium hydroxide	~~0,03~~ 0.03	~~0,05~~ 0.05	~~0,08~~ 0.08	~~0,10~~ 0.10
C)				
- Distilled water	~~10,00~~ 10.00	~~20,00~~ 20.00	~~19,00~~ 19.00	~~20,00~~ 20.00
- Sodium metaborate	~~0,20~~ 0.20	~~0,30~~ 0.30	~~0,40~~ 0.40	~~0,80~~ 0.80
- Calcium cyanamide	~~0,20~~ 0.20	~~0,35~~ 0.35	~~0,45~~ 0.45	~~0,90~~ 0.90

As already noted, specific ~~agent~~ composition will ~~be depended~~ depend on application conditions, agent in which it is used, etc. ~~Therefore, for example, for temperature of -25°C, additives from table "A" with 38% of basic substance (glycerol) are used, for temperature of -35°C formulation from table "A"/B with 48% of basic substance is prepared, for temperature of -55°C formulation from table "A"/C with 60% of basic substance is prepared and for temperatures above -65°C formulation from table "A"/D with 88% of basic substance is prepared. All these combinations are resistant temperatures from +110 to +160°C.~~

Afterwards, product is packed according to market and manufacturer demands. This product can be used immediately.

Here follows description of composition of anti-corrosion non-toxic inhibitor water solution, i.e., description of regenerator composition for wasted antifreeze. This composition is inhibitor for above said antifreeze and as such it is ingredient of that antifreeze. At the same time, this inhibitor is designed for use as modifier and regenerator for wasted antifreeze, and it extends antifreeze lifetime and refreshes anti-corrosive protection of wide variety of internal combustion engines and also other engines, heating and cooling systems. This inhibitor is used in small concentrations (from 8 to 12% by weight) for regeneration and modification of wasted antifreeze ~~from 8% - 12% by weight~~ in which it is poured, i.e., antifreeze with 10% - 18% of inhibitor.

~~Therefore, this~~ The invention provides aqueous concentrated anticorrosive formulation, which is suitable for use as additive for wasted fluid – antifreeze in engine cooling system. This invention enables extension of anti-corrosive protection lifetime for fluid/antifreeze in internal combustion engine cooling system. ~~Referred to inhibitory properties, it~~ It has great ability for anti-corrosive protection. This agent may be used as emulsifier and modifier.

It is very important that it is non-toxic ~~inhibitor~~. ~~Especially, advancement and effectiveness is represented by adding this~~ This inhibitor can be added in small amounts to the wasted antifreeze, relative to total weight of wasted antifreeze. This inhibitor is very potent. It regenerates wasted antifreeze, it is resistant to high boiling temperature, it lowers freezing point, has great ability for heating and cooling system anti-corrosive protection, bring alkaline stocks to satisfactory level and ~~rises~~ raises pH values. ~~Thereat, it~~ It can be used in any antifreeze, it is made of polycarboxylate, and it is soluble in alcohol, alcohol/water mixture and in water alone. It does not corrode[[,]] nor damage[[s]] cooling systems, and it is efficacious in ~~a small~~ low concentrations.

~~Namely, conventional fluids –~~ Conventional antifreeze solutions weaken due to ~~application~~ use. Their lifetime is very limited. In ~~drained~~ old antifreeze solutions, the pH value ~~lowers~~ decreases and ~~its~~ protection against corrosion becomes minimal or ceases.

~~Composition of anticorrosive agent – inhibitor water solution with particular additive type make, besides~~ Besides the additives indicated for the antifreeze composition, the following additives can be useful in the regenerator composition:

1. Glycerol
   - chemical formula $C_3H_8O_3$
   - ~~quality at least 98,0% (99,5%)~~ minimum purity of 98.0% (99.5%)

2. Water – soften or distilled

3. Benzotriazole ~~who is an~~ – effective ~~corrosion~~ inhibitor against corrosion of ~~all variety of~~ metals in neutral solution[[s.]]

4. ~~Three-ethanol-amine (three-ethile-amine~~ Triethanolamine ($(HOCH_2CH_2)_3N$) a corrosion inhibitor of iron and steel in water solutions.

5. ~~Sodium-tetraborate~~ Sodium tetraborate
   - chemical formula $Na_2B_4O_7$
   - an inhibitor ~~in composition of this formulation of~~ for several metals, aluminum and its alloys.

6. ~~Sodium-three-polyphosphate~~ Sodium tripolyphosphate
   - ~~applied for the protection of circular~~ protects circulating systems such as heat[[er]] exchangers from 4°~~C till~~ to 99°C. It's ~~efficient~~ effective as ~~the~~ an inhibitor ~~in~~ over a wide range of pH but not ~~bellow~~ below 6. ~~This additive isn't~~ Not toxic.

7. ~~Sodium-nitrate~~ Sodium nitrate
   - chemical formula $NaNO_3$
   - in formula composition protects several metals

8. ~~Sodium-nitrite~~ Sodium nitrite
   - chemical formula $NaNO_2$
   - necessary concentration depends on conditions of corrosion and water composition in formulation.

9. ~~Sodium-sulfide~~ Sodium sulfite
   - chemical formula ~~(without water~~ $NaSO_3$ (without water) or ~~(Na_2SO_3)$7H_2O$~~ $NaSO_3 \cdot 7H_2O$
   - ~~in this formulation~~ good corrosion inhibitor ~~of~~ for magnesium, aluminum and ~~its~~ their alloys in alkali environment and in water solution of glycerol.

10. ~~Potassium-sulfide~~ Potassium sulfate
    - chemical formula K_2SO_4
    - ~~quality~~ purity of at least 99%
    - ~~solution~~ [[–]] easily soluble in water
    - in this formulation inhibitor of aluminum, magnesium or its alloys.

11. Sodium [[–]] meta-silicate
    - ~~inhibitor~~ inhibits corrosion of aluminum in ~~water~~ aqueous solution of this formulation.

12. ~~Potassium dichromate~~ Potassium dichromate
    - ~~this additives is~~ used for metal protection in contact with antifreeze.

13. ~~Sodium – chromate~~ Sodium chromate
    - chemical formula in acids ~~HNO3, H3PO4 i H2SO4~~ (Na_2CrO_4)
    - inhibitor of corrosion of steel, cast iron, aluminum, copper, ~~zink,~~ zinc and brass in ~~water~~ aqueous solution of this formulation

14. ~~Sodium – benzoate~~ Sodium benzoate
    - chemical formula ~~C6H5SO6Na or (C7H5O2Na)~~ $C_7H_5O_2Na$
    - inhibitor of corrosion of steel in ~~water~~ aqueous solutions and ~~well maintained~~ maintains pH values and alkalis.

15. ~~Benzolsulphamide~~ Benzolsulfamide
    - chemical formula ~~C6H5SO2NH2~~ $C_6H_5SO_2NH_2$
    - inhibitor of corrosion of black metals
    - in this formulation also of other metals and their alloys

16. Calcium [[–]] cyanamide
    - in this formulation inhibitor of corrosion of steel in water solutions and salt solutions

17. ~~Sodium hydroxide~~ Sodium hydroxide
    - suitable for aluminum protection as well as for maintaining ~~of alkali reserve and pH~~ pH value ~~between~~ of 9-11

18. ~~Polimark polycarboxilate BASF,~~ Polycarboxylates which are soluble in water and alcohol solutions~~. In this invention marked~~ such as ~~SOKALON®~~ SOKALAN® CP-12S or CP-10. In this formulation, ~~the~~ ABC COBLEX's ~~policarboxilate in concentration is~~ polycarboxylates also ~~applicable~~ are useful.

19. Silicate oil

Therefore, ~~for purpose of~~ to maintain pH values ~~maintenance~~ between [[9,5-]] 9.5 and 11, silicates are used which are especially important for aluminum engines for protection of aluminum components in the cooling system[[,]] and also for ~~maintenance of alkaline stocks in patent~~ maintaining alkalinity of the fluid. The most important component for pH value maintenance is sodium hydroxide, which can be used at 0.5 to 10% ~~with 0,5-10%~~ by weight in solution.

~~Following table "B"~~ Table B shows different variants of anti-corrosive non-toxic inhibitor compositions and regenerator-modifier compositions for wasted antifreeze.

TABLE ~~"B"~~ B

FORMULATION	A		B		C	
Components (%)						
A)						
- Glycerol	~~82,95~~	82.95	~~75,65~~	75.65	~~63,55~~	63.55
- Distilled water	~~5,00~~	5.00	~~5,00~~	5.00	~~5,00~~	5.00
- ~~Polimark-p~~Polycarboxylate	~~1,0~~	1.0	~~1,30~~	1.30	~~1,60~~	1.60
- Benzotriazole	~~1,0~~	1.0	~~2,20~~	2.20	~~4,20~~	4.20
- Triethanolamine	~~0,80~~	0.80	~~1,10~~	1.10	~~1,60~~	1.60
- Sodium metasilicate	~~0,20~~	0.20	~~0,40~~	0.40	~~0,90~~	0.90
- Potassium dichromate	~~0,30~~	0.30	~~0,70~~	0.70	~~1,10~~	1.10
B)						
- Distilled water	~~5,00~~	5.00	~~5,00~~	5.00	~~5,00~~	5.00
- Sodium tetraborate (borax)	~~0,30~~	0.30	~~0,45~~	0.45	~~0,90~~	0.90
- Sodium nitrate	~~0,35~~	0.35	~~0,40~~	0.40	~~0,70~~	0.70
- Sodium nitrite	~~0,20~~	0.20	~~0,45~~	0.45	~~0,60~~	0.60
- Sodium ~~sulphide~~ sulfide	~~0,30~~	0.30	~~0,90~~	0.90	~~2,20~~	2.20
- Potassium~~-sulphide~~ sulfide	~~0,25~~	0.25	~~0,40~~	0.40	~~1,20~~	1.20
- Sodium[[-]]tripolyphosphate	~~0,20~~	0.20	~~0,60~~	0.60	~~0,75~~	0.75
- Sodium chromate	~~0,20~~	0.20	~~0,45~~	0.45	~~1,20~~	1.20
- Sodium benzoate	~~0,30~~	0.30	~~0,85~~	0.85	~~1,20~~	1.20
- Sodium hydroxide	~~0,03~~	0.03	~~0,05~~	0.05	~~0,08~~	0.08
C)						
- ~~Benzosulphamide~~ Benzosulfamide	~~0,30~~	0.30	~~0,45~~	0.45	~~1,00~~	1.00
- Calcium cyanamide	~~0,45~~	0.45	~~1,10~~	1.10	~~1,20~~	1.20
- Silicate (silicate oil)	~~0,005~~	0.005	~~0,005~~	0.005	~~0,005~~	0.005

Thus obtained regenerator is nontoxic.

~~There should be noted that for~~ For corrosion inhibition of all engine types, besides said inhibitors, monocarboxylic acids, and ~~polycaroxylates~~ polycarboxylates in relatively small concentrations are suitable. ~~Then~~ Also, azole compounds, including mercaptobenzotriazole,

benzotriazole salts, and polytriazole salts ~~are~~ can be included. ~~The preferred~~ Preferred are nitrate salts, nitrite salts, and mixtures thereof. ~~Then~~ Also, phosphates may be used which are useful for corrosion inhibition, as is polycarboxylate.

Improved stable polycarboxylate type is based on ~~polycrylic~~ polyacrylic acid or polymaleic acid. These polycarboxylates are compatible with other components as in process for obtaining ~~as~~ and in subsequent fluid utilization. Examples for polycarboxylates which can be used are those which are produced ~~in German firm~~ by BASF under the trade name ~~SOKALON~~ SOKALAN. These are polycarboxylates which are available ~~in~~ as water solutions. This ~~inhibitor~~ additive generally may be used in formulation from ~~0,01%~~ 0.01 to 10%, but it is preferred from ~~0,01%~~ 0.01 to about ~~0,1%~~ 0.1% (by weight). ~~This additive may be purchased under the trade name SOKALON® CP-12S or CP-10.~~

Process for obtaining is conducted in the reactor (container) by heating and cooling ~~and keeping~~ to maintain constant temperature between 80°-90°C. Mixing process after the heating takes about 1 h. ~~In this~~ This process uses 20-40% distilled (softened) water, 20-30% propylene glycol, 10-20% polyvalent alcohol (glycerol) ~~measured~~ and other inhibitor components. After that, follows cooling and packing according to market needs.

This regenerator for antifreeze is tested by modified method in 3 X 3 ASTM method and in DIN and by using DIN method. Additionally, standard test method for corrosion in engine coolant in glass vessel is used, with corrosive solution.

BRIEF REVIEW OF ANTIFREEZE AND REGENERATOR FOR WASTED ANTIFREEZE TESTS

a) Antifreeze composition is tested and metal sample purification procedure is conducted according to modified ASTM specification.

At required temperature, 30-33% of corrosive water is used according to ASTM. All changes are weighted in mg, and they meet the standards.

Table 1[[.]]

	Allowed (ASTM)	Finding
Copper	5	~~-0,8~~ -0.8
Solder	10	~~+0,6~~ +0.6
Brass	10	~~-0,6~~ -0.6
Iron	5	~~+0,2~~ +0.2
Gray smelting	5	~~-2,4~~ -2.4
Aluminum	10	~~-5,0~~ -5.0

Findings from ASTM tests from ~~table~~ Table 1 meet the standard.

b) Analogous corrosion tests

b1) Corrosion: coupons weight loss (the most mg)

Table 2[[.]]

	Allowed (ASTM)	Finding
Copper	5	~~-0,6~~ -0.6
Solder	10	~~+0,1~~ +0.1
Brass	10	~~-0,6~~ -0.6
Iron	5	~~+0,1~~ +0.1
Gray smelting	5	~~-2,3~~ -2.3
Aluminum	10	~~-5,9~~ -5.9

Findings are obtained according to modified ASTM ~~METHOD~~ method. Findings meet the standard.

b2) Corrosion: coupons weight loss, the most mg (JUS H.Z8.O56)

Table 3[[.]]

	Allowed (ASTM)	Finding
Copper	5	~~+1,9~~ +1.9
Solder	10	~~+1,8~~ +1.8
Brass	10	~~+2,7~~ +2.7
Iron	5	~~+3,4~~ +3.4
Gray smelting	5	~~+3,7~~ +3.7
Aluminum	10	~~+4,0~~ +4.0

Findings are obtained according to analogous method by JUS HZ8.O56 in glass vial with corrosive liquid 30%, and antifreeze 1:1 for temperature -18°C.

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~~**BRIEF REVIEW OF ANTIFREEZE AND REGENERATOR TESTS**~~

Herein described antifreeze (i.e., anti-freezing and anti-corrosive agent) which is obtained by using regenerator for wasted antifreeze (with inhibitor), and regenerator alone, have been subjected to the following analyses:

1. Examination by University in Novi Sad, Faculty for technical science, laboratory for physical-technical and solar measurements in 1988 and 1989. Findings meet TUB, ASTM and DIN standards.

2. ~~The extremely~~ An extreme exploitation test ~~has been~~ was performed for this antifreeze and regenerator~~, by~~ on metallic coupons ~~processing trough their purification~~, ~~and test was~~ conducted according to modified ASTM method and specification. In such a way plates were installed in the cooling systems of ~~the~~ General Motors engines: Pontiac ~~2.300~~ 2300 cc[[,]] and 3100 ~~Pontiac 3.100~~ cc, 1991 models, Chevrolet Corsica ~~3.100~~ 3100 KW and Beretta ~~2.300~~ 2300 cc, 1991 models. Coupons were used in ~~exploitation test with~~ vehicles ~~driving~~ driven during winter and summer period at external temperatures of -15°C and between +35°-40°C. Between ~~5.000~~ 5,000 and ~~20.000~~ 20,000 km were passed in these tests~~.~~ ~~Exploitation was tested~~ with normal driving, as in common everyday car driving.

According to this examination results were obtained as in ~~the table~~ Table 4 (exploitation method).

~~Tabela~~ Table 4[[.]]

	Allowed	Finding Corsica	Finding Beretta	Finding Pontiac 2300 ~~cca~~	Finding Pontiac 3100 ~~cca~~
Copper	5	~~-1,2~~ -1.2	~~-1,2~~ -1.2	~~+2,4~~ +2.4	~~+1,9~~ +1.9
Solder	10	~~-2,4~~ -2.4	~~-2,4~~ -2.4	~~-0,5~~ -0.5	~~+1,8~~ +1.8
Brass	10	~~-0,2~~ -0.2	~~-0,2~~ -0.2	~~+0,6~~ +0.6	~~+2,0~~ +2.0
Iron	5	~~+0,6~~ +0.6	~~+0,6~~ +0.6	~~+1,4~~ +1.4	~~+8,6~~ +8.6
Gray smelting	5	~~+3,4~~ +3.4	~~+3,4~~ +3.4	~~+3,6~~ +3.6	~~+6,1~~ +6.1
Aluminum	10	~~+3,7~~ +3.7	~~+3,7~~ +3.7	~~+6,1~~ +6.1	~~+3,6~~ +3.6

~~Exploitation method:~~ Corsica 3100 cc[[,]] passed ~~7.000~~ 7,000 km; ~~table 5,~~ Beretta 2300 cc[[,]] passed ~~5.000~~ 5,000 km; ~~table 6,~~ Pontiac 2300 cc[[,]] passed ~~10.000~~ 10,000 km; and ~~table 7,~~ Pontiac 3100 cc[[,]] passed ~~20.000~~ 20,000 km. In all the vehicles coupons ~~have been~~ were installed for 8 months. Coupons were installed in the cooling systems at the highest gravitation pressure. For example, water pump operating pressure was at an average about 1 kPa. Average engine operating temperature was about +110°C. After coupons were removed, coupons were processed according to ASTM standard.

Findings indicate that this antifreeze is in accordance with high ASTM standard and ~~it is~~ satisfactory ~~guarantee~~ for all the engines in which it is used in their cooling systems, and not only in warranty period, but above ~~300.000~~ 300,000 km and after 6 years of engine exploitation.

PATENT CLAIMS

1. Non-toxic anti-freezing and anti-corrosion water solution comprising polyvalent alcohol such as glycerol from 38% to 88%, water and additives as inhibitors which is effective at temperatures from -65°C to +110°C.

2. Non-toxic anti-freezing and anti-corrosion water solution according to claim 1, for temperatures up to -25°C., which is comprised of water solution of additives plus glycerol, where water solution of additives comprises 97.40% of distilled water, 0.60% of triethanolamine, 0.60% of polycarboxylate, 0.50% of benzotriazole, 0.20% of sodium tetraborate; 0.20% of sodium nitrate, 0.15% of sodium nitrite, 0.10% of sodium sulphide; 0.13% of potassium sulphide, 0.10% of Sodium chromate, 0.10% of Sodium benzoate, 0.03% of Sodium hydroxide, 0.20% of Sodium metaborate, 0.20% of calcium cyanamide, 0.005% of silicate oil, and where glycerol makes 38% of final non-toxic anti-freezing and anti-corrosion water solution.

3. Non-toxic anti-freezing and anti-corrosion water solution according to claim 1, for temperatures up to -35°C., which is comprised of water solution of additives plus glycerol, where water solution of additives comprises 92.0% of distilled water, 1.00% of triethanolamine, 1.00% of polycarboxylate, 1.50% of benzotriazole, 0.40% of sodium tetraborate, 0.30% of sodium nitrate, 0.25% of sodium nitrite, 0.25% of sodium sulphide, 0.90% of potassium sulphide, 0.20% of Sodium chromate, 0.20% of Sodium benzoate, 0.05% of Sodium hydroxide, 0.30% of Sodium metaborate, 0.35% of calcium cyanamide, 0.005% of silicate oil, and where glycerol makes 48% of final non-toxic anti-freezing and anti-corrosion water solution.

4. Nontoxic anti-freezing and anti-corrosion water solution according to claim , for temperatures up to -55°C., which is comprised of water solution of additives plus glycerol, where water solution of additives comprises 82.0% of distilled water, 3.10% of triethanolamine, 2.60% of polycarboxylate, 3.20% of benzotriazole, 0.60% of sodium tetraborate, 0.40% of sodium nitrate; 0.35% of sodium nitrite, 1.10% of sodium sulphide; 2.20% of potassium sulphide; 0.65%

of Sodium chromate, 0.35% of Sodium benzoate 0.08% of Sodium hydroxide, 0.40% of Sodium metaborate, 0.45% of calcium cyanamide, 0.005% of silicate oil, and where glycerol makes 60% of final non-toxic anti-freezing and anti-corrosion water solution.

5. Non-toxic anti-freezing and anti-corrosion water solution according to claim 1, for temperatures up to 65°C., which is comprised of water solution of additives plus glycerol, where water solution of additives comprises 78.00% of distilled water, 3.60% of triethanolamine, 3.40% of polycarboxylate, 4.80% of benzotriazole, 0.80% of sodium tetraborate, 0.45% of sodium nitrate, 0.45% of sodium nitrite, 1.40% of sodium sulphide, 2.90% of potassium sulphide, 1.00% of Sodium chromate 0.45% of Sodium benzoate, 0.10% of Sodium hydroxide, 0.80% of Sodium metaborate, 0.90% of calcium cyanamide, 0.005% of silicate oil, and where glycerol makes 88% of final non-toxic anti-freezing and anti-corrosion water solution.

6. Regenerator for wasted antifreeze which comprises polyvalent alcohol such as glycerol water and additives as inhibitors.

7. Regenerator for wasted antifreeze, which comprises 82.95% of glycerol 10.00% of distilled water, 1.00% of polimark polycarboxylate, 1.00% of benzotriazole, 0.80% of triethanolamine, 0.20% of sodium metasilicate, 0.30% of potassium dichromate, 0.30% of sodium tetraborate (borax), 0.35% of sodium nitrate, 0.20% of sodium nitrite, 0.30% of sodium sulphide, 0.25% of potassium sulphide, 0.20% of sodium tripolyphosphate, 0.20% of sodium chromate, 0.30% of sodium benzoate, 0.03% of sodium hydroxide, 0.30% of benzosulphamide, 0.45% of calcium cyanamide and 0.005% of silicate (silicate oil).

8. Regenerator for wasted antifreeze, which comprises 75.65% of glycerol, 10.00% of distilled water, 1.30% of polimark polycarboxylate 2.20% of benzotriazole, 1.10% of triethanolamine, 0.40% of sodium metasilicate, 0.70% of potassium dichromate, 0.45% of sodium tetraborate (borax), 0.40% of sodium nitrate, 0.45% of sodium nitrite, 0.90% of sodium sulphide, 0.40% of potassium sulphide, 0.60% of sodium tripolpyhosphate, 0.45% of sodium

chromate, 0.85% of sodium benzoate, 0.05% of sodium hydroxide, 0.45% of benzosulphamide, 1.10% of calcium cyanamide and 0.005% of silicate (silicate oil).

9. Regenerator for wasted antifreeze, which comprises 63.55% of glycerol 10.00% of distilled water, 1.60% of polimark polycarboxylate, 4.20% of benzotriazole 1.60% of triethanolamine, 0.90% of sodium metasilicate, 1.10% of potassium dichromate, 0.90% of sodium tetraborate (borax), 0.70% of sodium nitrate, 0.60% of sodium nitrite, 2.20% of sodium sulphide, 1.20% of potassium sulphide, 0.75% of sodium tripolyphosphate, 1.20% of sodium chromate, 1.20% of sodium benzoate, 0.08% of sodium hydroxide, 1.00% of benzosulphamide, 1.20% of calcium cyanamide and 0.005% of silicate (silicate oil).

ABSTRACT

~~It is a~~ A nontoxic liquid for cooling of all types of engines[[,]] provides anticorrosive protection, has a boiling point over 130°C, has a freezing point ~~over~~ of at least -40°C, ~~it's~~ and is not harmful to people, animals and plants. The inhibitors and additives ~~make the~~ provide basic protection against freezing and corrosion in engine. The additives are compatible with the additives for cooling systems recommended by some vehicle and ~~motors~~ motor producers, like Chrysler, General Motors, and Ford~~, so this coolant meets and exceeds their demands~~. ~~The basic substance and additives are given in description patent. The Formulation of Nontoxic liquid Watery Solution Against Freezing and Corrosion (table "A") as well as the chemical formulas. When the inhibitor from the patent The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze is used into the basic substance glycerol-water), the inhibitor is added in 10-15% of weight part. Such a product is applicable immediately.~~